

Measurement Challenges for Carbon Nanotube Material

Edward Sosa¹, Sivaram Arepalli¹, Pasha Nikolaev¹, Olga Gorelik¹
and Leonard Yowell²

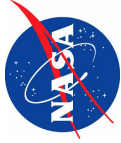
¹ *ERC Inc. / NASA - Johnson Space Center, Houston, TX*

² *NASA - Johnson Space Center, Houston, TX*

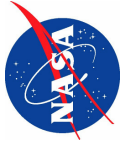
Abstract

The advances in large scale applications of carbon nanotubes demand a reliable supply of raw and processed materials. It is imperative to have a consistent quality control of these nanomaterials to distinguish material inconsistency from the modifications induced by processing of nanotubes for any application. NASA Johnson Space Center realized this need five years back and started a program to standardize the characterization methods. The JSC team conducted two workshops (2003 and 2005) in collaboration with NIST focusing on purity and dispersion measurement issues of carbon nanotubes [1]. In 2004, the NASA-JSC protocol was developed by combining analytical techniques of SEM, TEM, UV-VIS-NIR absorption, Raman, and TGA [2]. This protocol is routinely used by several researchers across the world as a first step in characterizing raw and purified carbon nanotubes. A suggested practice guide consisting of detailed chapters on TGA, Raman, electron microscopy and NIR absorption is in the final stages and is undergoing revisions with input from the nanotube community [3]. The possible addition of other techniques such as XPS, and ICP to the existing protocol will be presented. Recent activities at ANSI and ISO towards implementing these protocols as nanotube characterization standards will be discussed.

- Ref.: 1) <http://mmptdpublic.jsc.nasa.gov/jscnano/>
2) Arepalli S., Nikolaev P., Gorelik O., Hadjiev V. G., Holmes W. A., Files B. S., and Yowell L., "Protocol for the Characterization of Single-Wall Carbon Nanotube Material Quality", Carbon, Vol. 42, pp. 1783-1791 (2004).
3) http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide.htm



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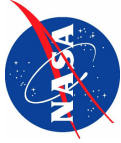
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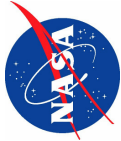
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**NIST Workshop on Instrumentation, Metrology, and Standards
for Nanomanufacturing**

Oct. 17-19, 2006, Gaithersburg, MD



OUTLINE



Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion

Study of fine variations in harvested material

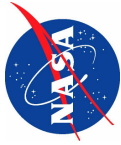
-Laser, arc and CVD production chambers

Additions to NASA-JSC protocol

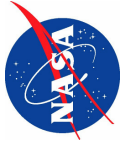
-Non-nanotube carbon and nanodispersion

Nanotube characterization standards

Future Work



QUESTIONS



Why do we need material quality assessment?

What do we have to know?

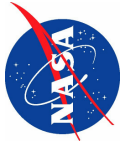
How do we perform the characterization?

How much time and money can we spend?

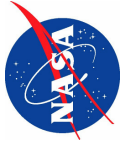
How many times do we need to do?

What else do we have to know about the production source, i.e. laser, arc, CVD, etc.?

.....????????

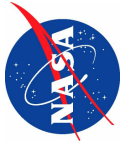


Material Quality = Purity?

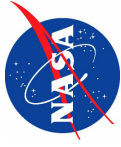


Why Do We Want to Know Nanotube Purity?

- Over the years, various manufacturers claimed purity anywhere from 50 to 90%. Do we trust these numbers?
What are we buying?
- How consistent is NT material produced by the same manufacturer in different batches?
- What are implications of nanotube purity in applications?
- How does the purity affect stress transfer in composites, electrical and thermal conductivity, surface area, sidewall chemistry, dispersion properties, etc.?



SWCNT Measurement Challenges



Current state of reliability and uncertainty

→ **NASA-JSC protocol for purity and dispersion**

Study of fine variations in harvested material

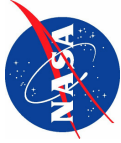
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Additions to NASA-JSC protocol

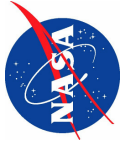
- Non-nanotube carbon and nanodispersion

Nanotube characterization standards

Future Work



How do We Perform Characterization?



Macroscopic

- Thermal Gravimetric Analysis (TGA)
- UV-Visible-Near Infrared (UV-Vis-NIR) Absorption
- NIR Fluorescence
- Inductively Coupled Plasma (ICP)
- Optical Microscopy
- Dynamic Light Scattering (DLS)
- X-ray Diffraction (XRD), SAXS, SANS
- Resistivity
- Surface Area(BET)
- Tensile Strength
- Thermal Conductivity

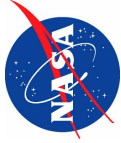
Microscopic

- Scanning Electron Microscopy (SEM)
- Energy Dispersive X-ray Analysis (EDX)
- Raman Spectroscopy
- X-ray Photoelectron Spectroscopy (XPS)

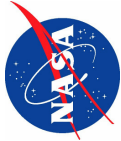
Nanosopic

- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscopy (STM)

Purity and Dispersion



NASA-JSC Protocol for Purity and Dispersion*

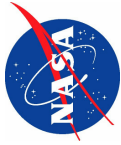


- To be able to directly compare nanotube samples of different origin, purified by different techniques.
- To gather as much information as possible about specimen **purity (non-nanotube carbon impurities and metal content)**, **dispersability** and **homogeneity**.
- To minimize time and effort spent on characterization.
- To optimize data collection to provide reliable assessment.

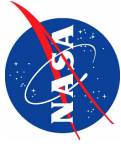
Available tools:

- Thermogravimetric analysis (TGA), (TA SDT 2960)
- Transmission electron microscopy (TEM) + EDS, (JEOL 2010 FX)
- Scanning electron microscopy (SEM) +EDS (Phillips XL40 FEG)
- Raman spectroscopy (Renishaw RM 1000)
- UV-Visible spectrometry (Perkin-Elmer Lambda 900)

* Ref: “NASA-JSC Protocol”; Carbon, Vol. 42, pp. 1783-1791 (2004)



SWCNT Measurement Challenges



Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion



Study of fine variations in harvested material

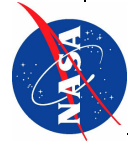
-Laser, arc and CVD production chambers

Additions to NASA-JSC protocol

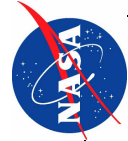
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Nanotube characterization standards

Future Work

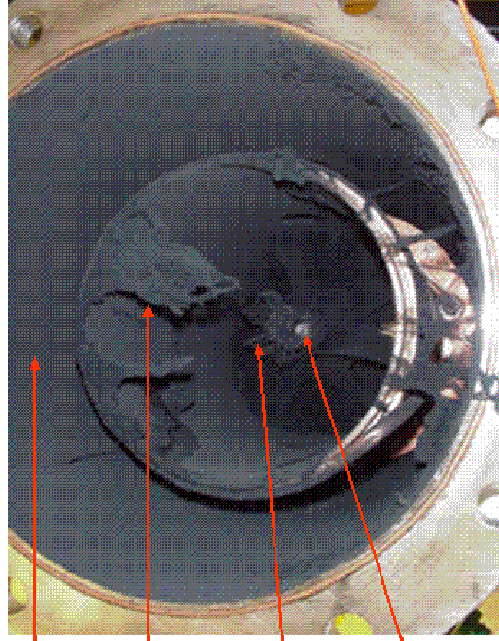


Material Variability with Production Source?



Production and Collection

Arc Discharge Method



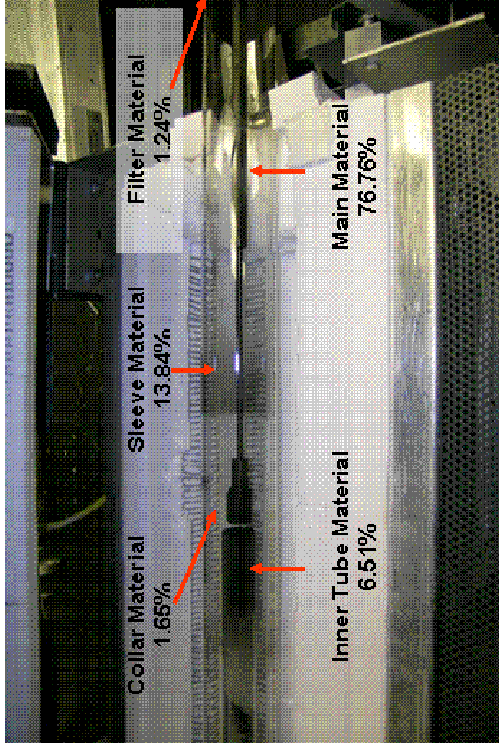
Wall Deposit

Webs

Collarette

Cathode

Pulsed Laser Vaporization



Collar Material
1.65%

Sleeve Material
13.84%

Filter Material
1.24%

Inner Tube Material
6.51%

Main Material
76.76%

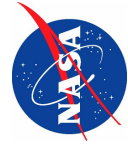
Arc Production Conditions:

3.92%Ni:1%Y, Pressure:506 Torr, Voltage:38.2V, Current:101.5A,

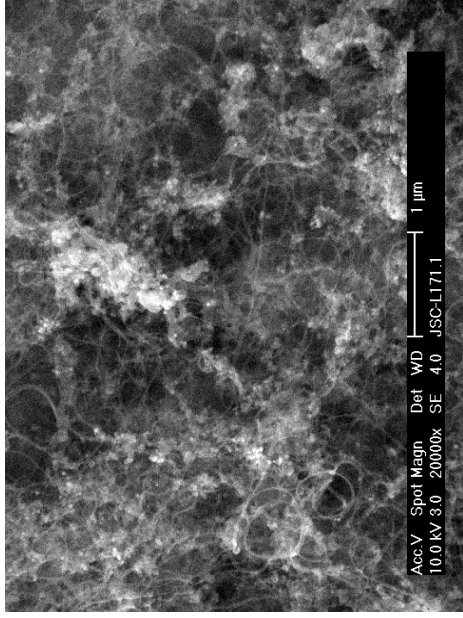
Electrode Distance:3 mm, Automated

Laser Production Conditions:

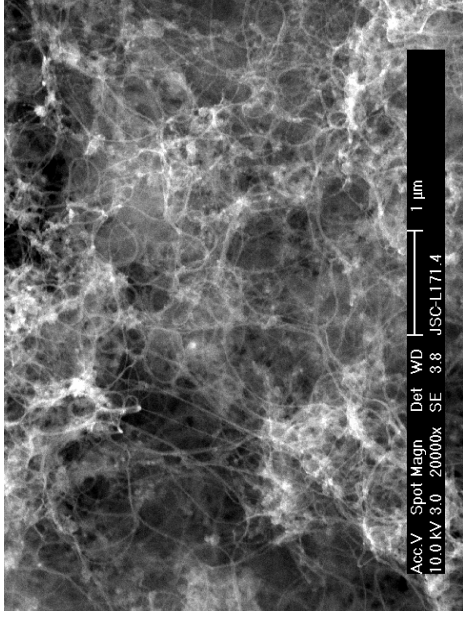
$\frac{3}{4}$ " diameter target, 1%Co:1%Ni, Pressure: 500T, Ar Flow Rate: 100 sccm, Pulse Separation: 50 ns , Power Density: 1.6J/cm², Oven Temperature: 1200 °C, Laser Sequence: Green-IR



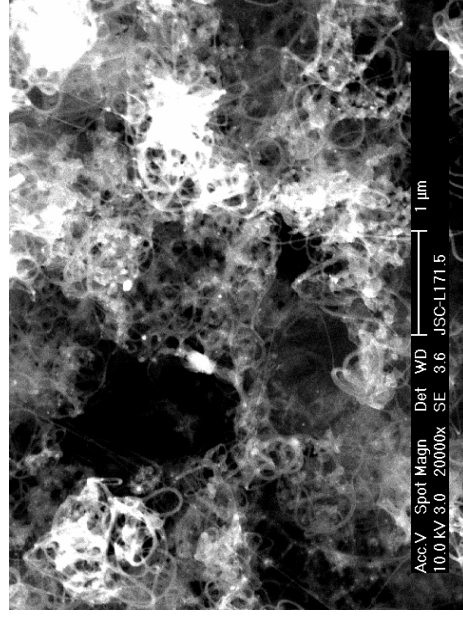
Laser Run #171; Morphology



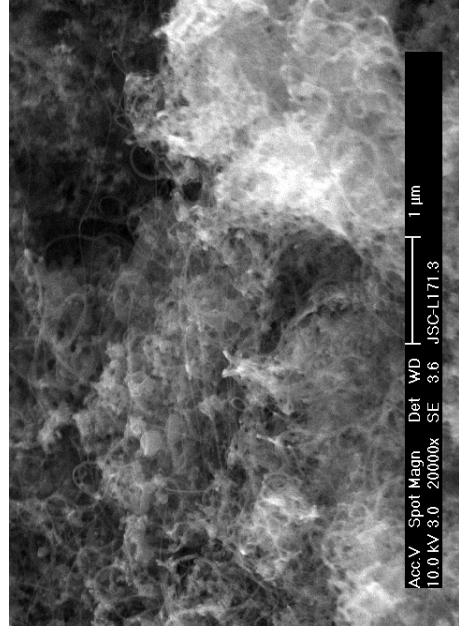
Collar



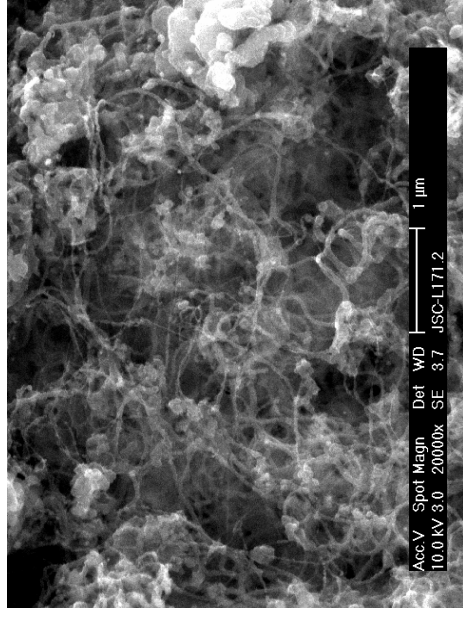
Sleeve



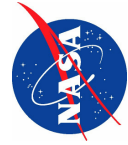
Main Material



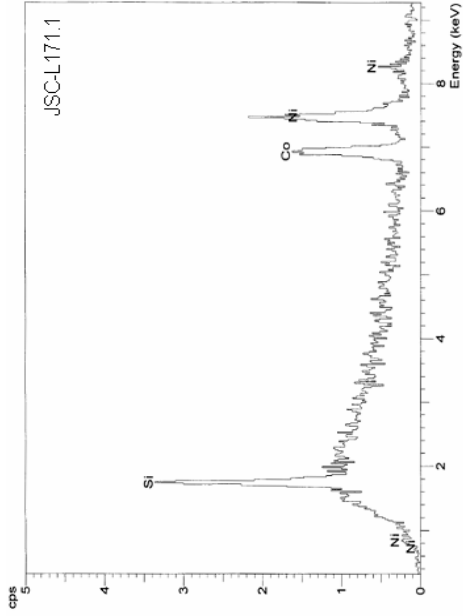
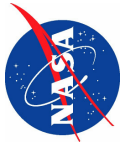
Filter



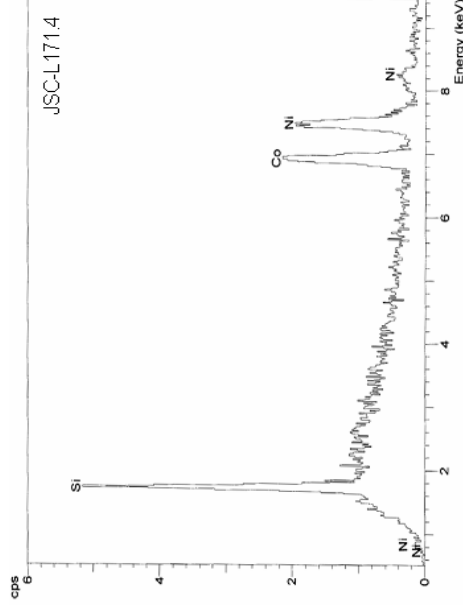
Inner Flow Tube



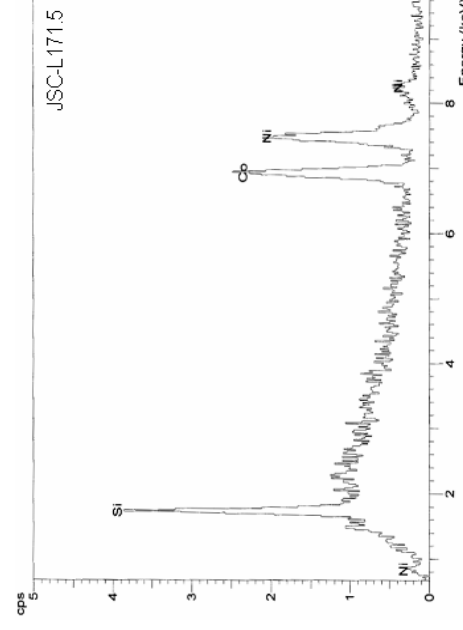
Laser Run #171; Purity by EDX



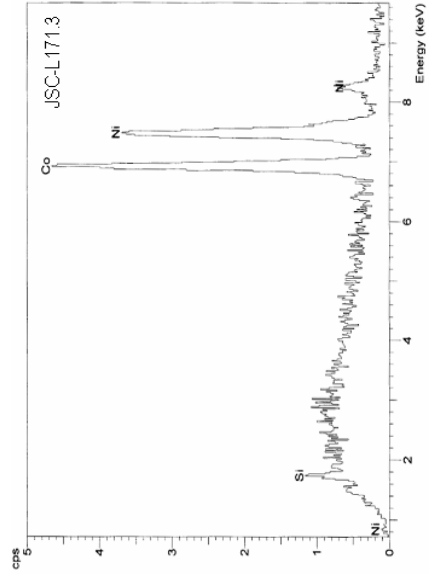
Collar



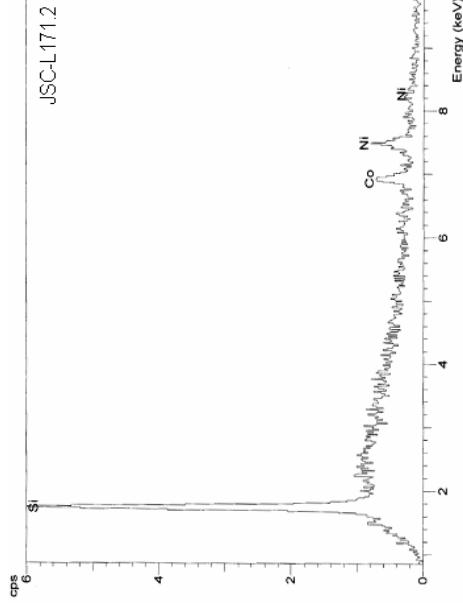
Sleeve



Main Material



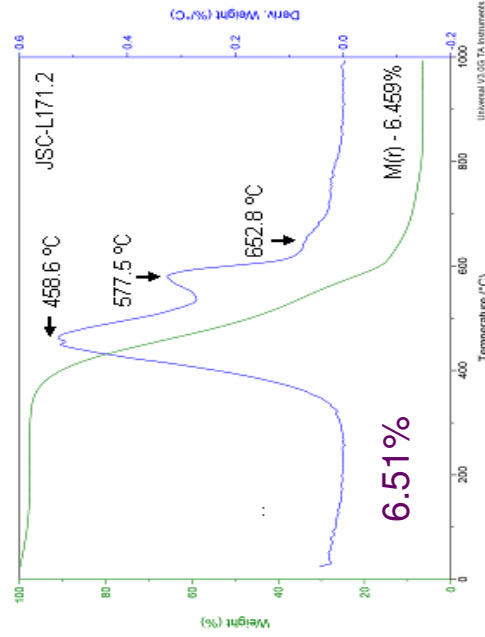
Filter



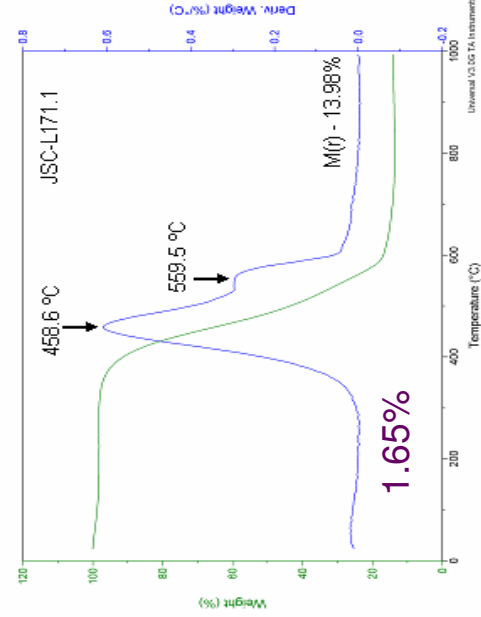
Inner Flow Tube



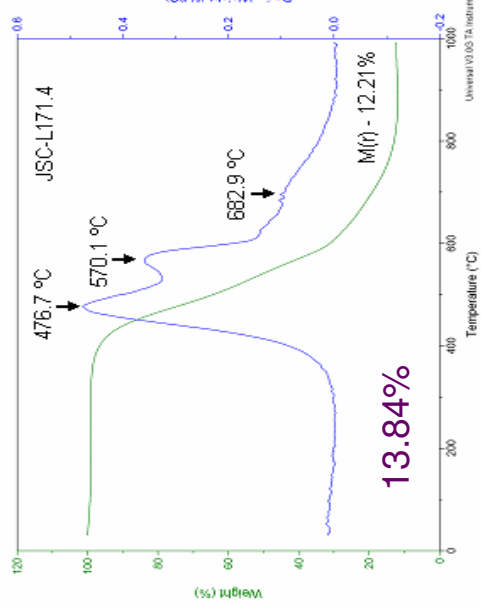
Harvested Laser Material: TGA Spectra



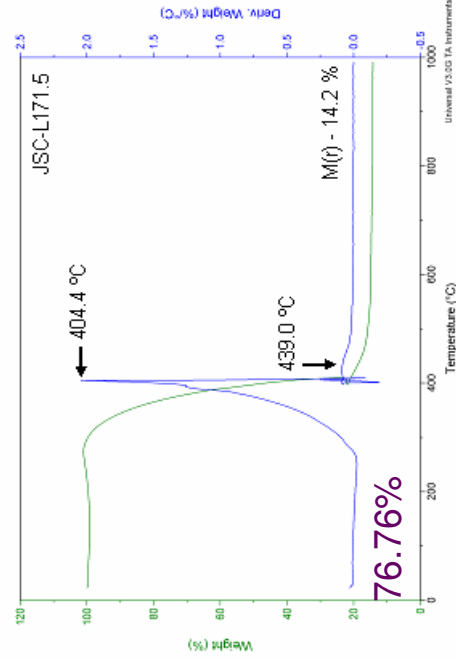
Inner Flow Tube



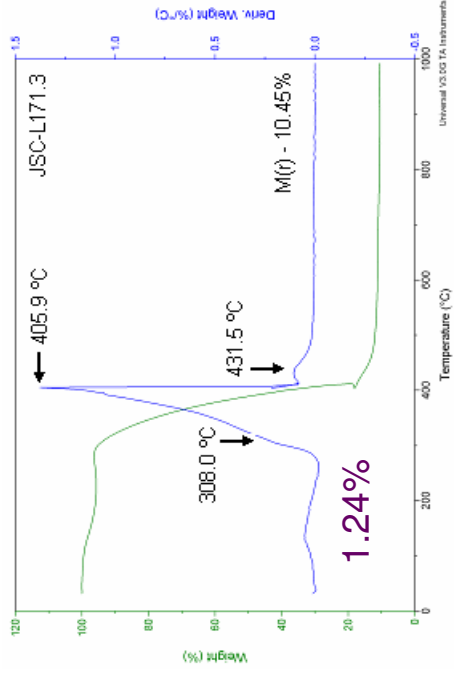
Collar



Sleeve

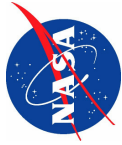


Main Material

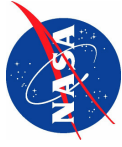


Filter

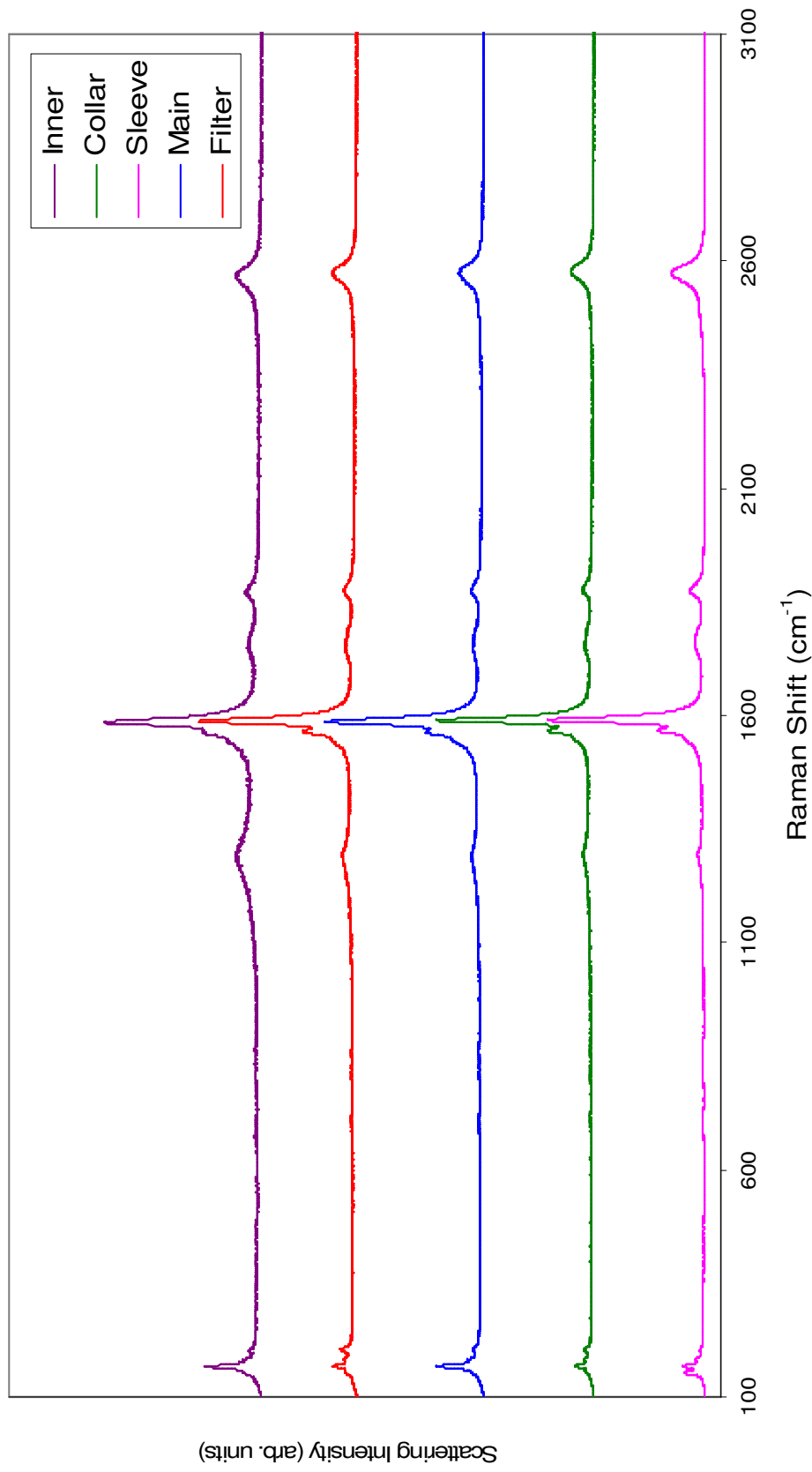
* Indicates the percentage of material weight collected *

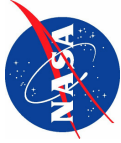


Harvested Laser Material: Raman Spectra

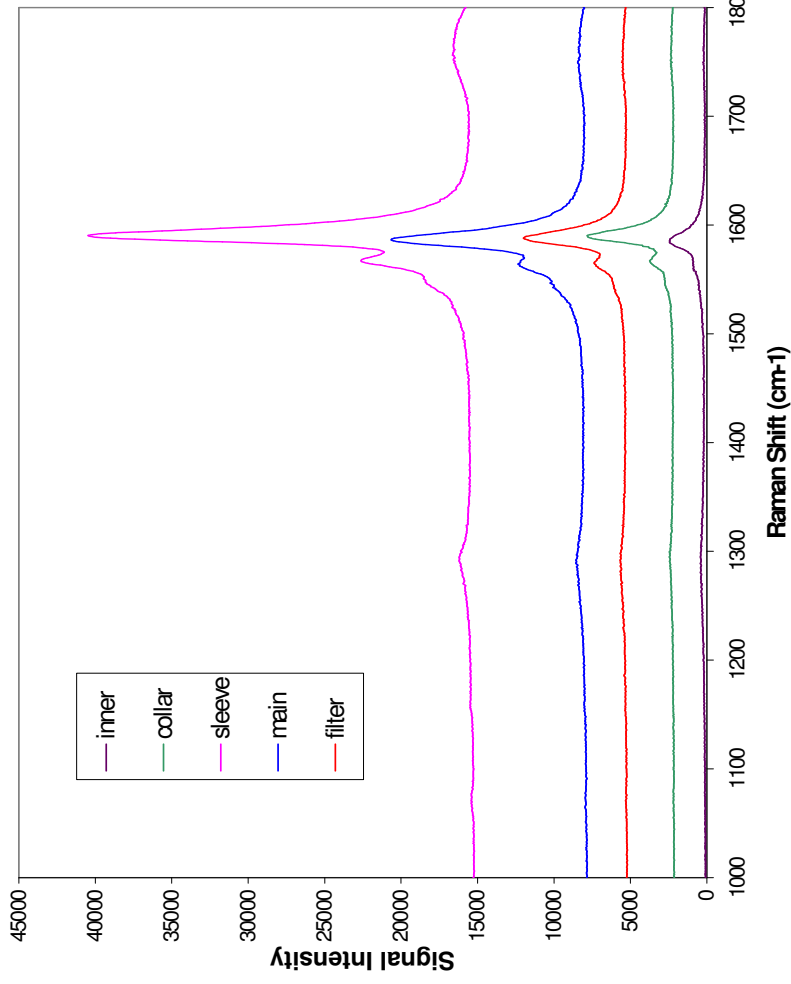
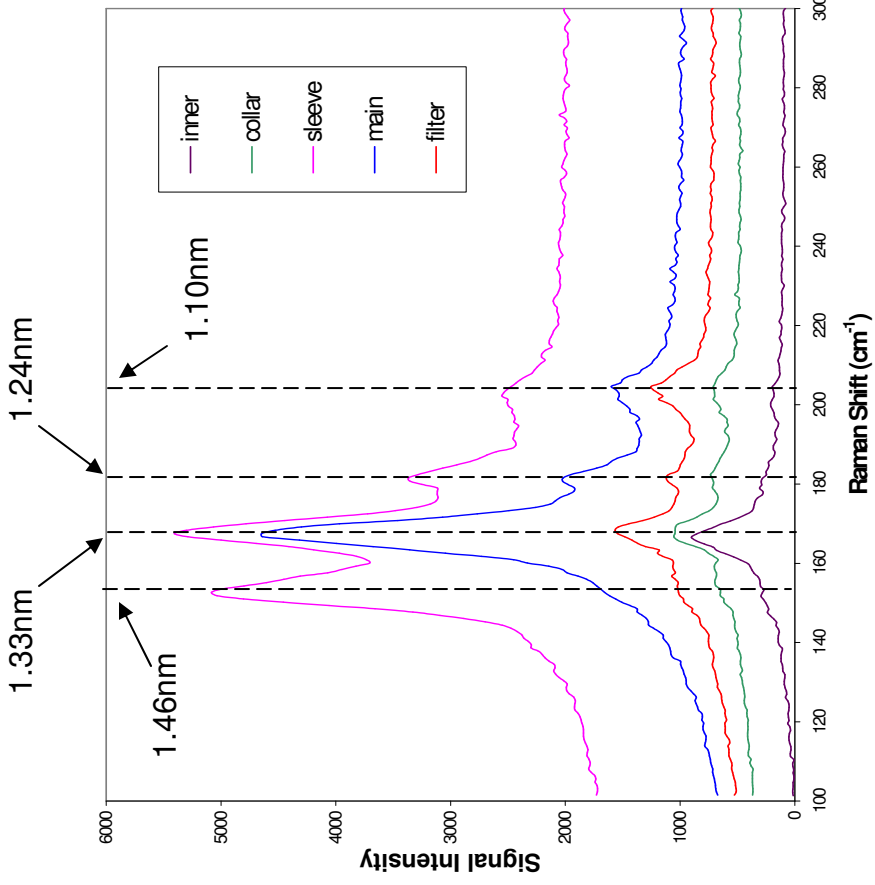


Laser Variability - Normalized Spectra





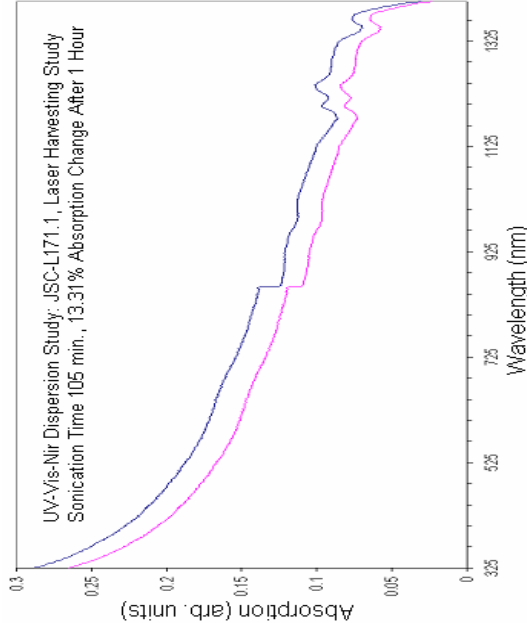
Laser Material: Raman Spectra (contd.)



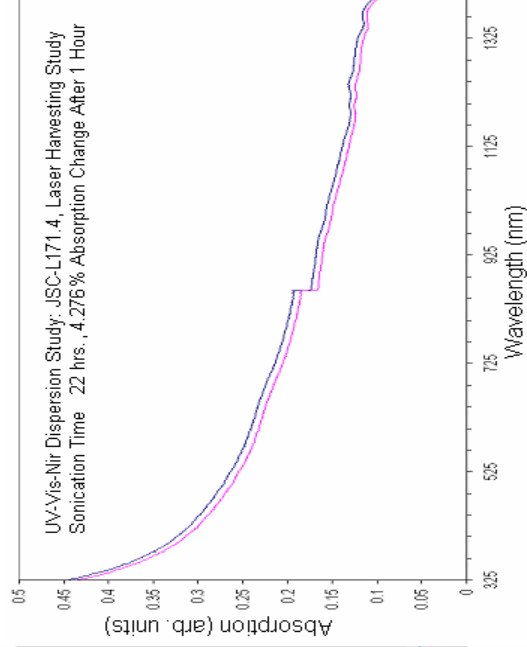
$$\omega_{\text{RBM}} = \alpha/d + b, \quad \alpha = \text{constant} = 223.5 \text{ cm}^{-1} \cdot \text{nm}$$
$$b = \text{intertube interactions} = 12.5 \text{ cm}^{-1}$$



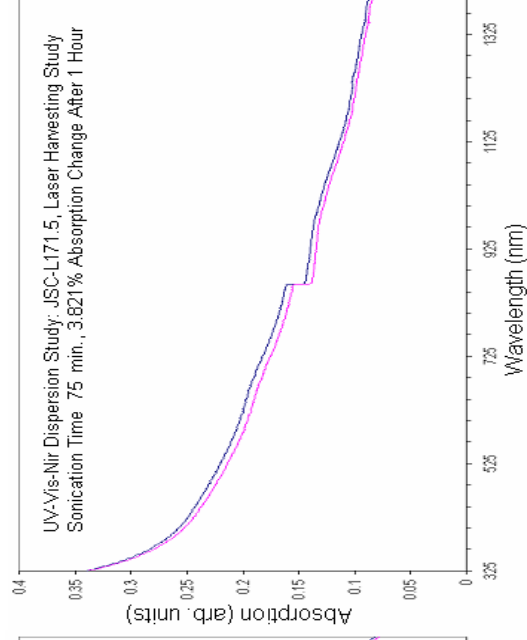
Harvested Laser Material: UV-Vis-NIR Spectra



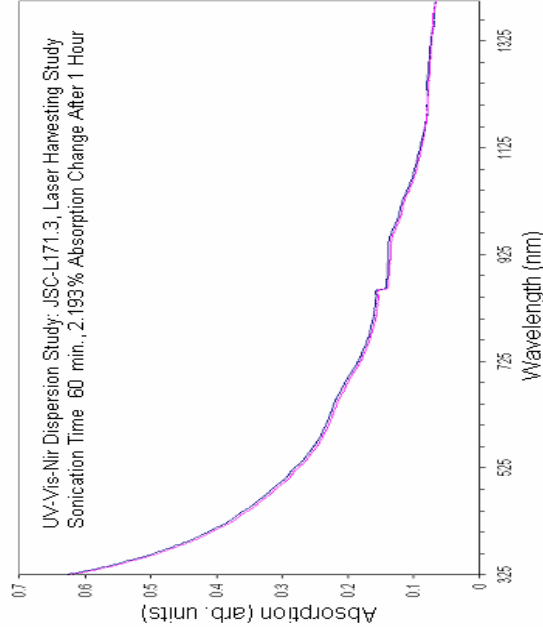
Collar



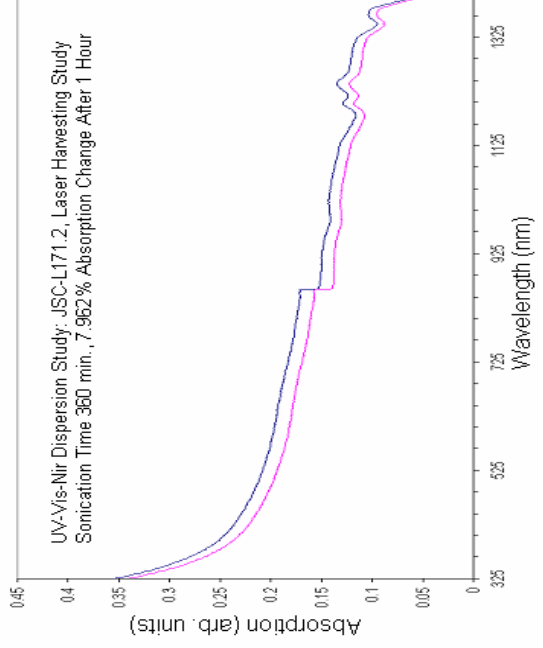
Sleeve



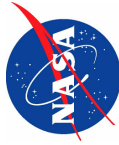
Main



Filter



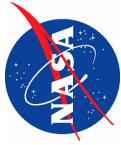
Inner Flow Tube



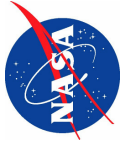
PROPERTIES

MATERIAL

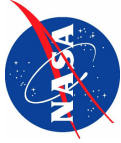
	Inner	Collar	Sleeve	Main	Filter
Residual Mass	6.45%	13.98%	12.21%	14.26%	10.45%
Thermal Stability	<u>Min</u> 458.6 °C <u>Max</u> 652.8 °C	<u>Min</u> 458.6 °C <u>Max</u> 559.5 °C	<u>Min</u> 476.7 °C <u>Max</u> 682.9 °C	<u>Min</u> 404.4 °C <u>Max</u> 439.0 °C	<u>Min</u> 405.9 °C <u>Max</u> 431.5 °C
Dispersion	7.962%	13.31%	4.276%	3.821%	2.193%
D/G Ratios	0.288	0.090	0.047	0.094	0.124
D-Band Position	1285.45cm ⁻¹	1289.9cm ⁻¹	1287.87cm ⁻¹	1284.84cm ⁻¹	1283.17cm ⁻¹
Small Diameter %	8.02%	22.6%	8.17%	9.85%	27.5%



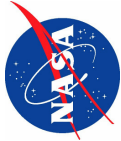
Laser Material Variability: Conclusions



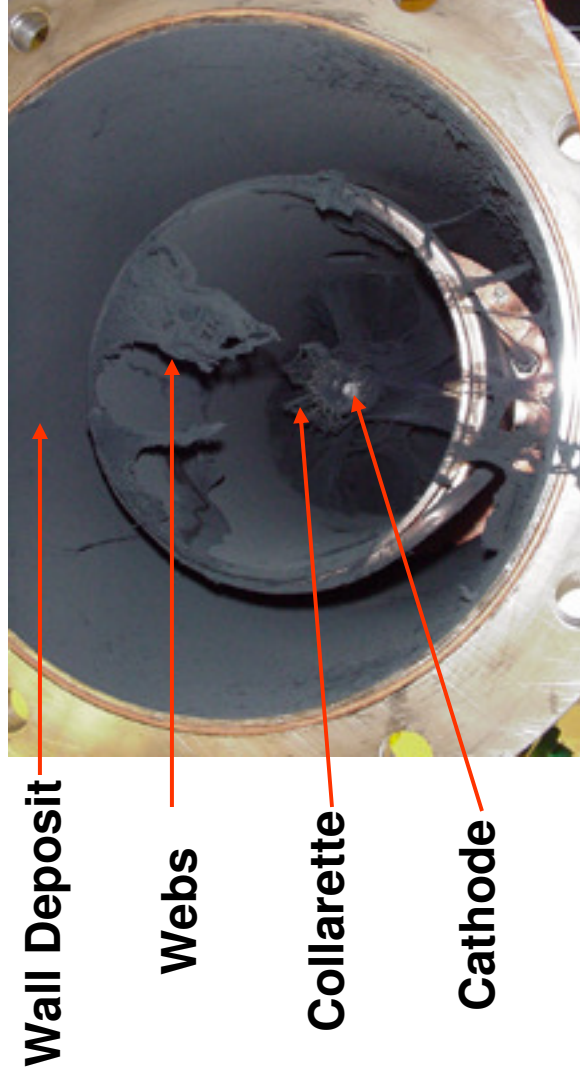
- Downstream SWCNT material tends to have lower thermal stability
- TGA spectral shape similar for main and filter SWCNT material. Inner tube material has half the residual mass compared to other materials.
- Downstream material is less crystalline (?) and more fluffy (TGA and UV-Vis-NIR)
- Spectral features in UV-Vis-NIR data is directly proportional to distance from target
- Percent Absorption change is inversely proportional to distance from target

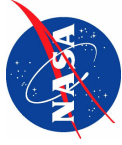


Variability Study of Harvested Arc Material

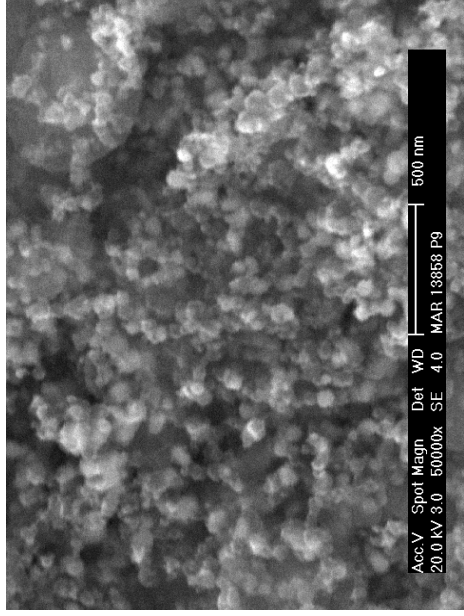
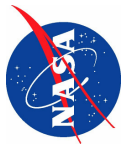


- Harvested Arc Material deposited on the cathode, collarette, webs and chamber wall.
- Characterized using JSC Protocol for SEM, TGA, UV-Vis and Raman

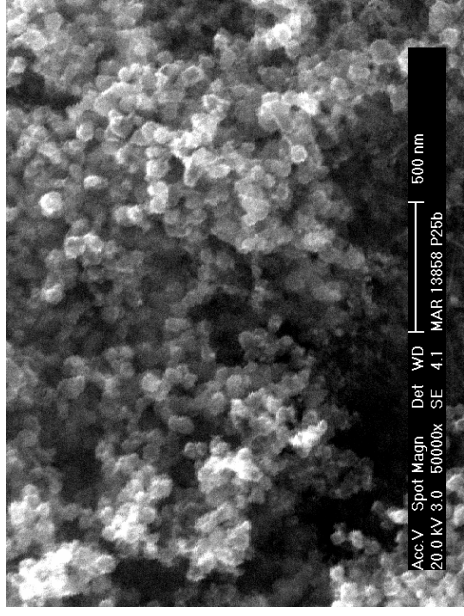




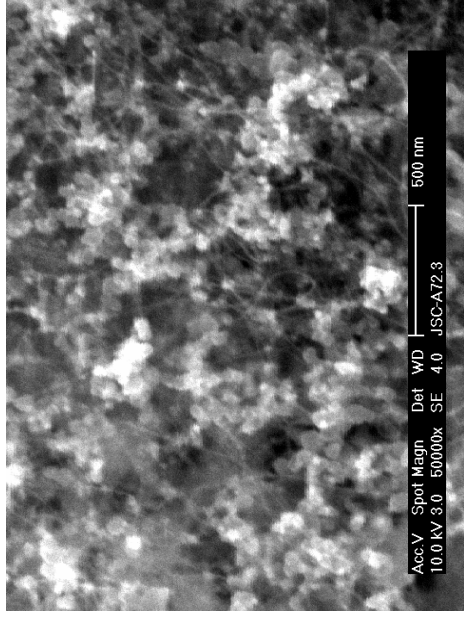
Harvested Arc Material: SEM and EDX



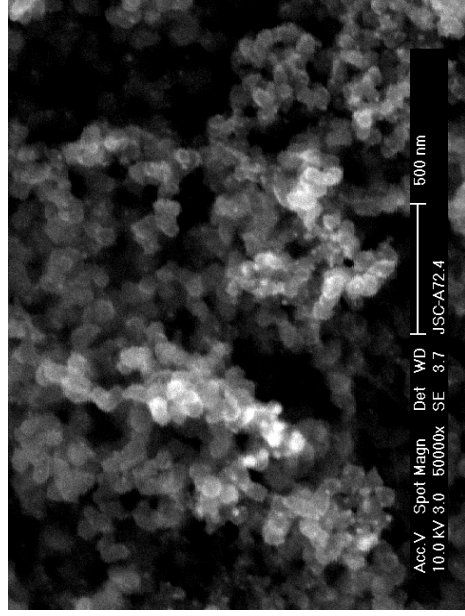
Cathode (JSC-A72.2)



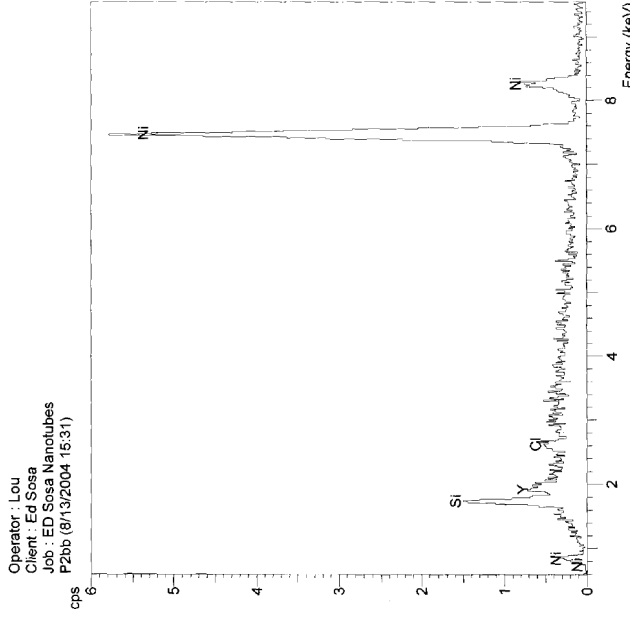
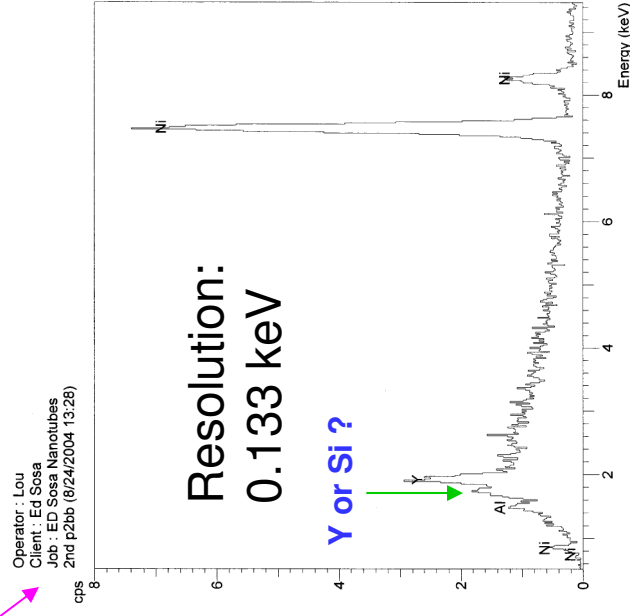
Collarette (JSC-A72.1)

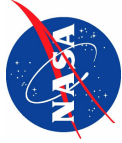


Webs (JSC-A72.3)

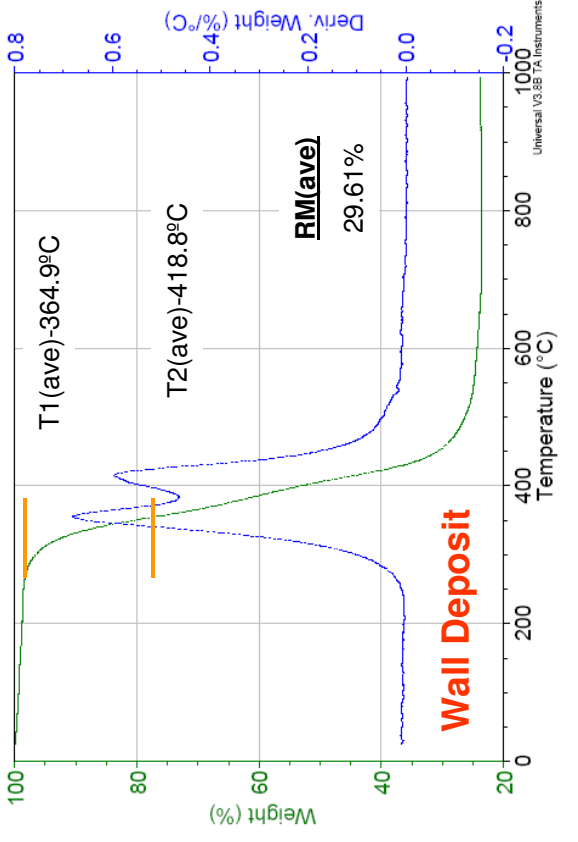
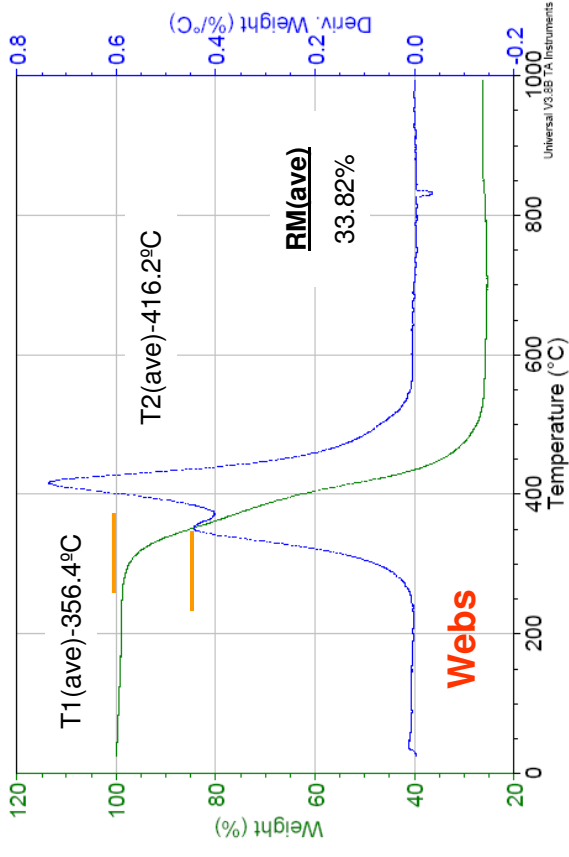
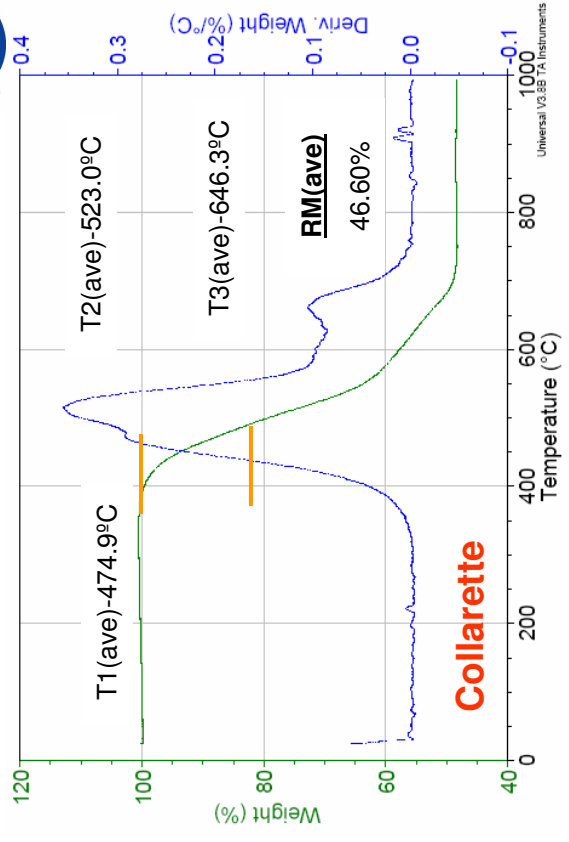
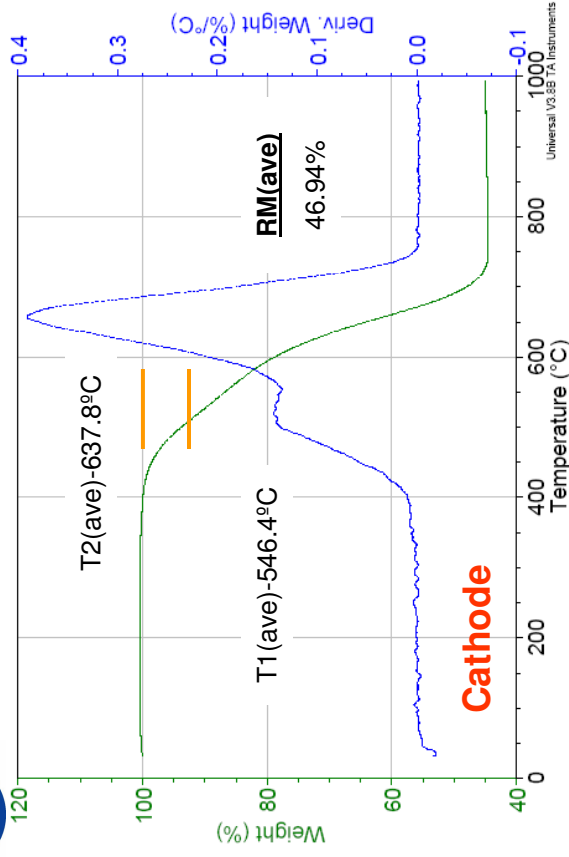
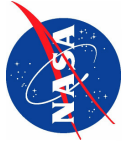


Wall Deposit (JSC-A72.4)

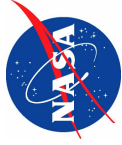




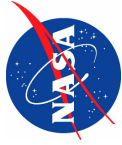
Harvested Arc Material: TGA Spectra



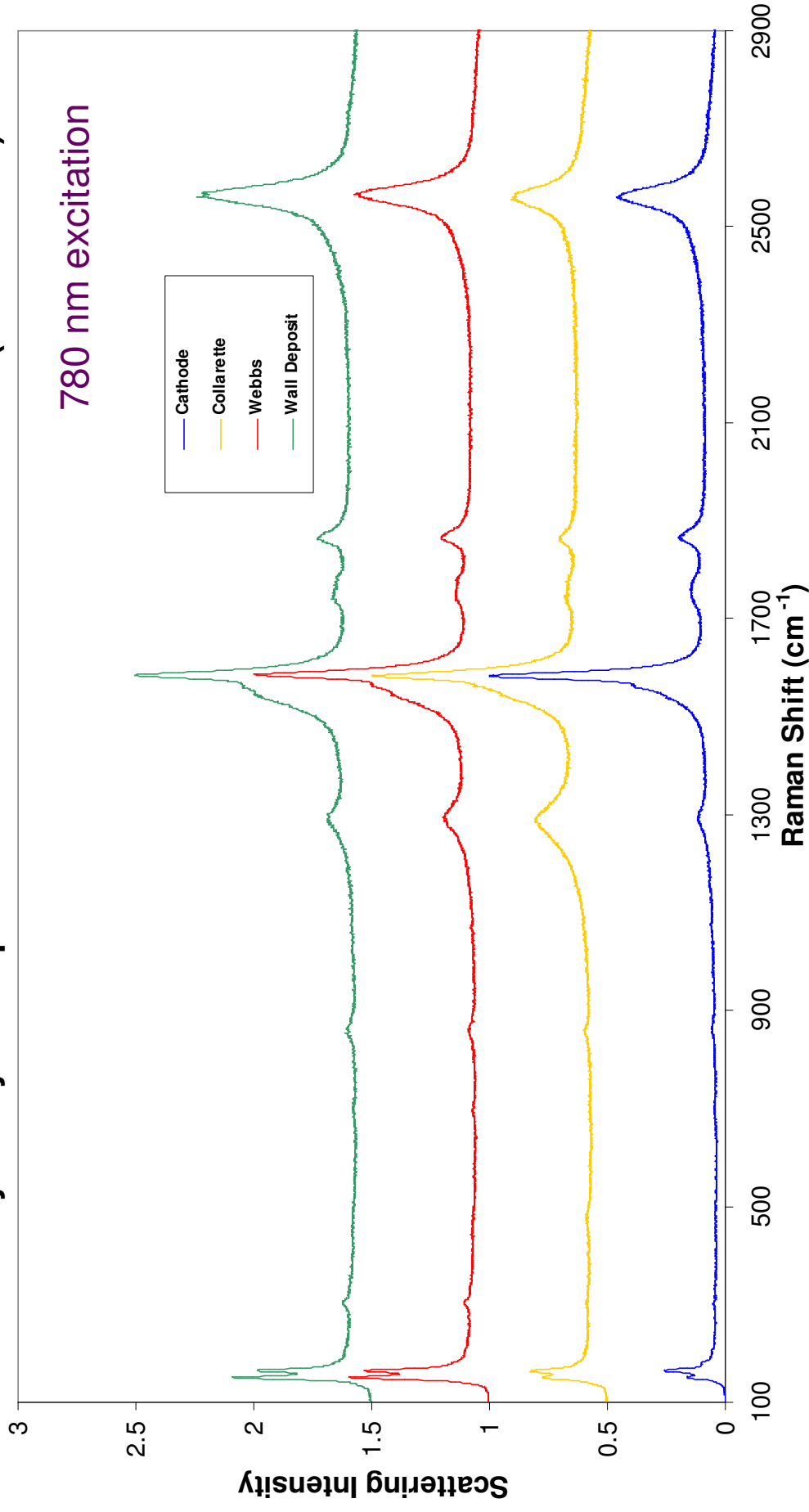
Possible causes for the variation: 1. Over-coating of metals 2. Tube diameters



Harvested Arc Material: Raman Spectra



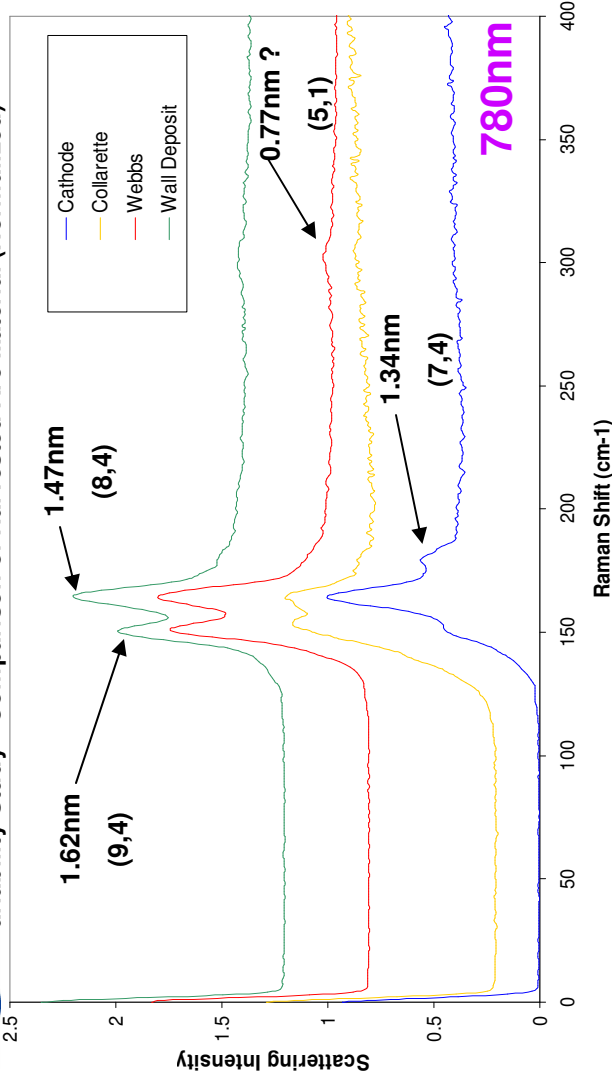
Variability Study - Comparison of Harvested Arc Material (Normalized)





Arc Material: Raman Spectra (contd.)

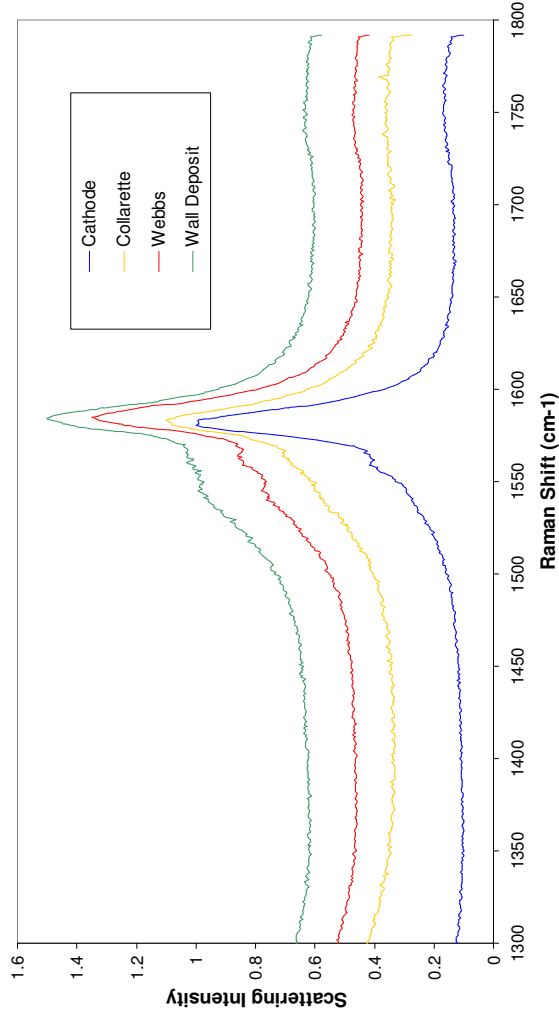
Variability Study - Comparison of Harvested Arc Material (Normalized)



Material deposited further away from electrodes have larger contribution of larger diameter tubes.

$$D_{\text{web}} > D_{\text{wall}} > D_{\text{col}} > D_{\text{cat}}$$

Variability Study - Comparison of Harvested Arc Material (Normalized)



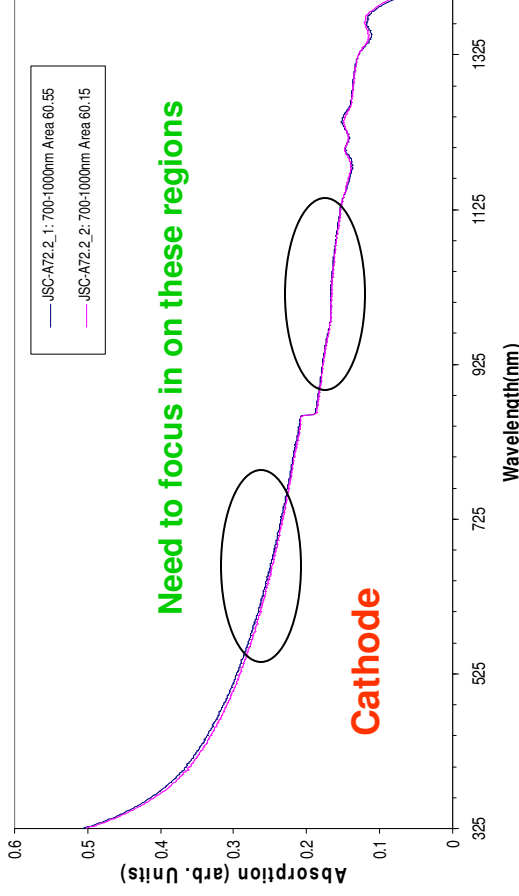
G-band agrees with diameter fractions – webs and wall deposit have higher fraction of larger diameters.



Harvested Arc Material: UV-Vis-NIR Spectra

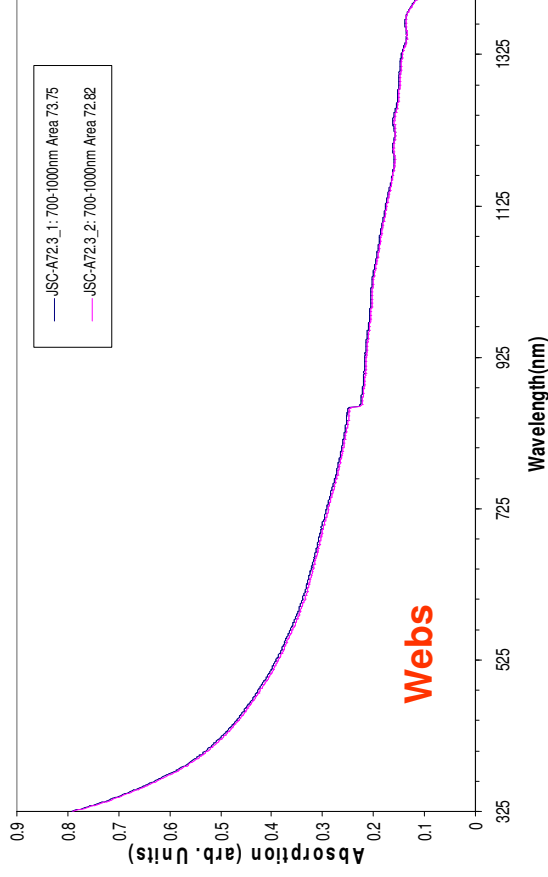
UV-VIS Dispersion Study : JSC-A72.2

JSC Arc unpurified-Harvesting Study, 120 min. Sonication, 0.6665% Change After 1 Hour



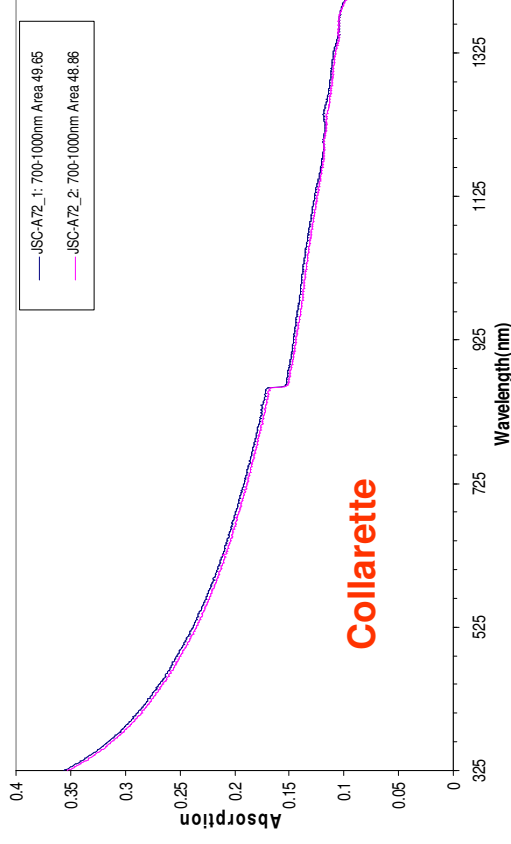
UV-VIS Dispersion Study : JSC-A72.3

JSC Arc unpurified-Harvesting Study, 30 min. Sonication, 1.265% Change After 1 Hour



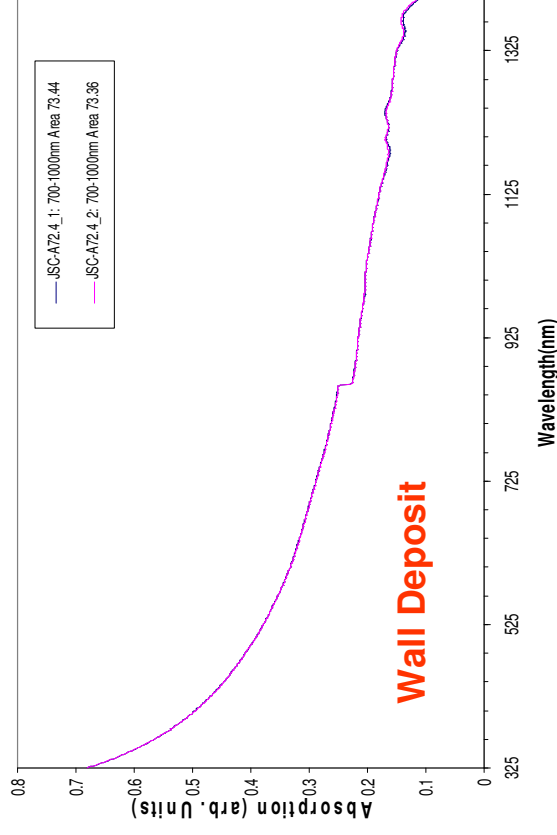
UV-VIS Dispersion Study : JSC-A72.1

Arc unpurified, 15min Sonication, 1.595% Change After 1 Hour



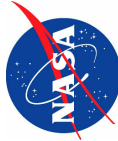
UV-VIS Dispersion Study : JSC-A72.4

JSC Arc unpurified-Harvesting Study, 30 min. Sonication, 0.1114% Change After 1 Hour





Arc Material Collection Variability Summary



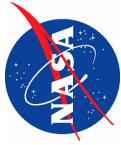
Arc Material:

Collection Region

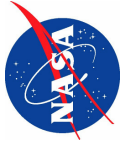
Cathode **Collarette** **Webs** **Wall Deposit**

Residual Mass (ave)	46.95%	46.60%	33.82%	29.61%
Thermal Stability (ave)	<div>Min 458.8 °C</div> <div>Max 637.8 °C</div>	<div>Min 474.9 °C</div> <div>Max 646.6 °C</div>	<div>Min 356.4 °C</div> <div>Max 416.2 °C</div>	<div>Min 364.9 °C</div> <div>Max 418.8 °C</div>
Dispersion	0.6665%	1.595%	1.265%	0.114%
D/G Ratios	0.0337	0.1655	0.0873	0.0438
Small Diameter % (Raman)	20.9%	8.87%	5.39%	4.97%

Properties



Arc Material Variability: Conclusions



TGA:

Lower oxidation temps for material further from electrodes more likely due to some degree of over-coating.

Lower metal content observed inversely to distance from electrodes.

Raman:

D-band does not support TGA carbon impurity speculation.

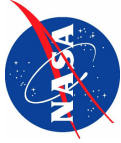
RBM suggests smaller diameters more prevalent in cathode materials.

G-band may show more metallic features in cathode material, while more SC features in wall deposit.

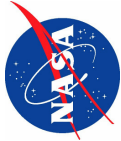
UV-Vis:

Suppressed optical features support over-coating of tubes.

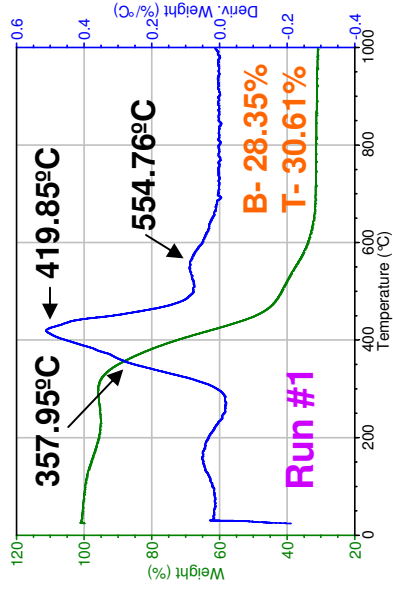
Stronger S22 transition in agreement with Raman results.



HiPco Material Variability Study -TGA

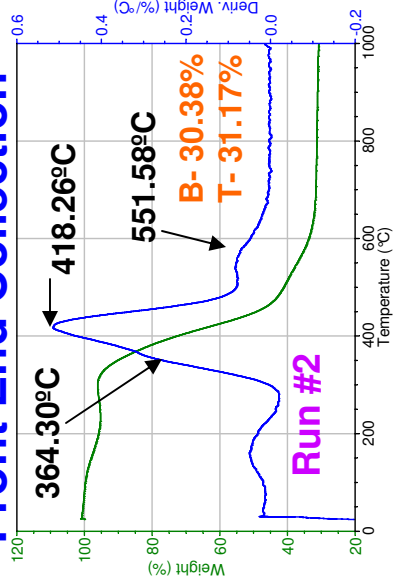


Size: 2.8339 mg

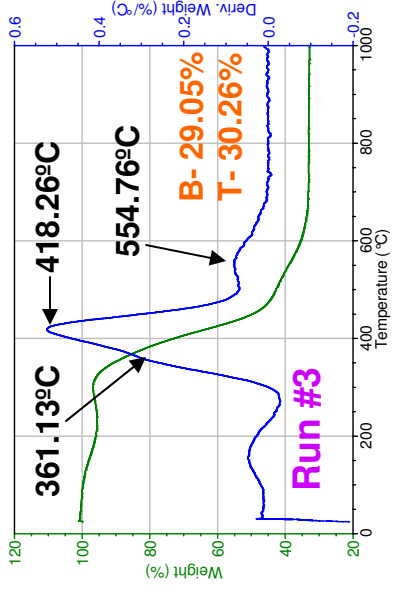


Size: 2.8339 mg

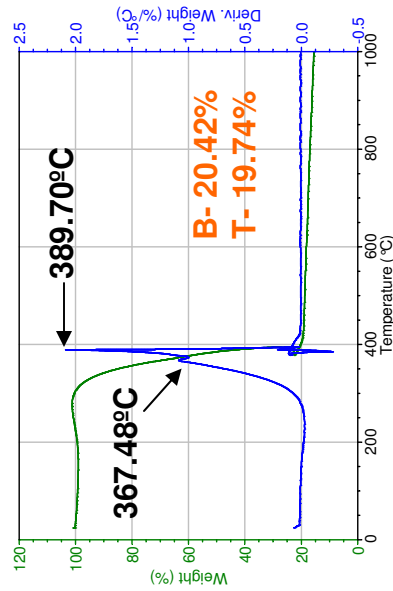
Front End Collection



Size: 2.9741 mg

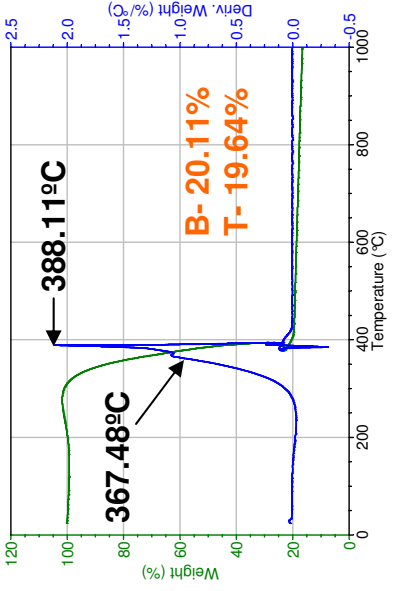


Size: 2.9427 mg

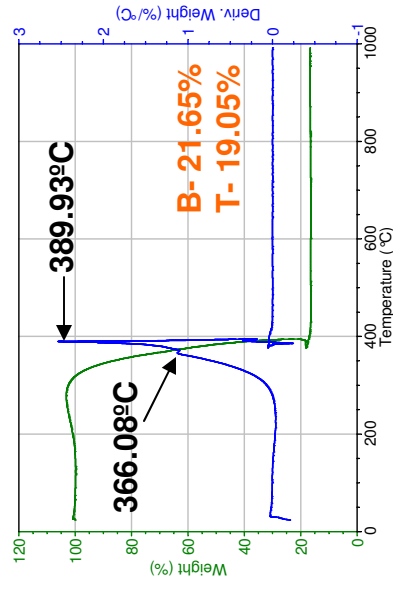


Size: 2.9427 mg

Back End Collection

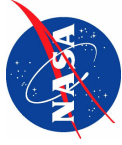


Size: 2.8549 mg

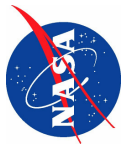


Results:

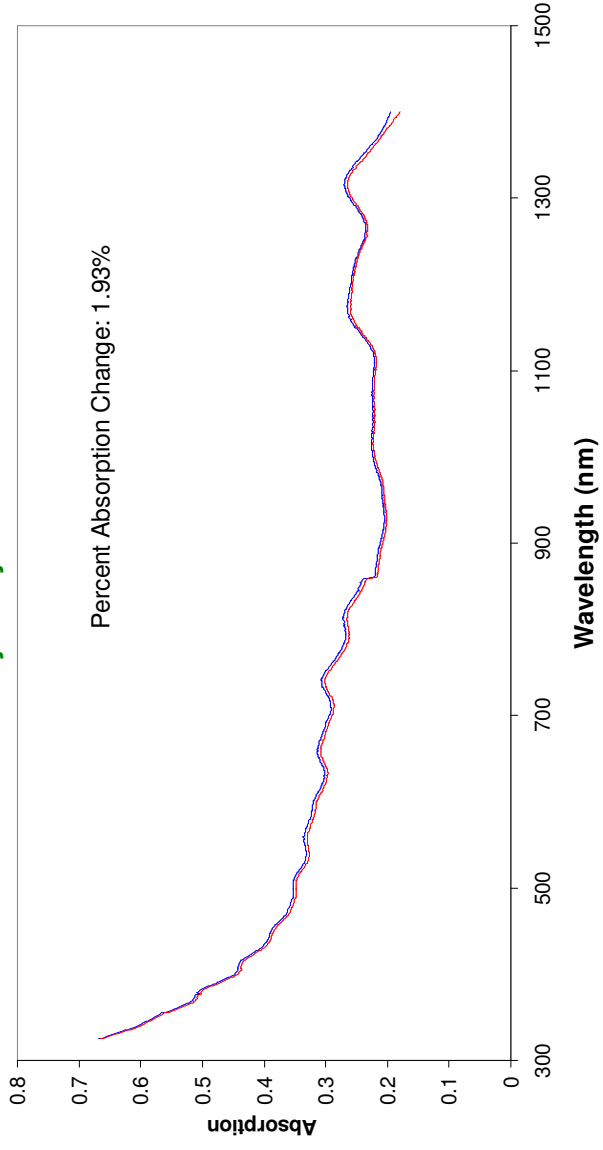
1. Both Materials show good homogeneity from consistent TGA spectra
2. Back end material displays combusive behavior
3. Back end material has ~33% less non-carbon impurities



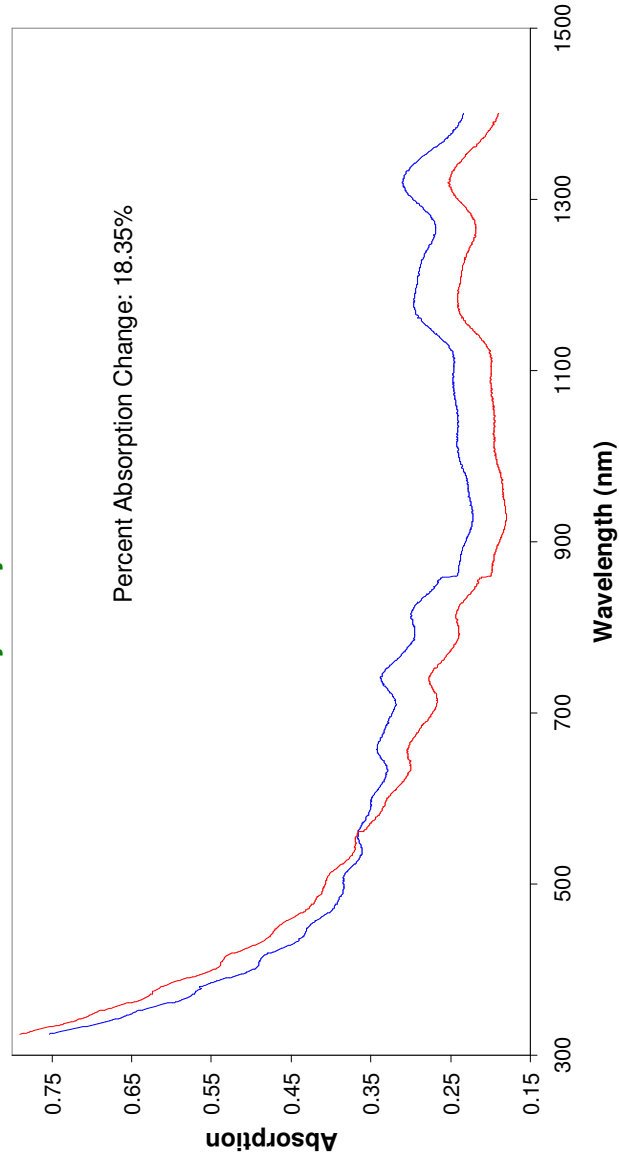
HiPco Material Variability Study: UV-Vis-NIR

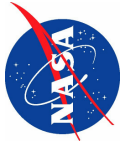


HiPco Variability Study - Front End Material

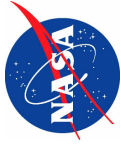


HiPco Variability Study - Back End Material





SWCNT Measurement Challenges



Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion

Study of fine variations in harvested material

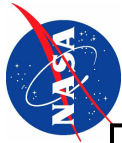
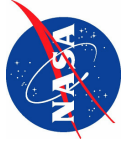
-Laser, arc and CVD production chambers

→ **Additions to NASA-JSC protocol**

-‘Non-nanotube’ carbon and nanodispersion

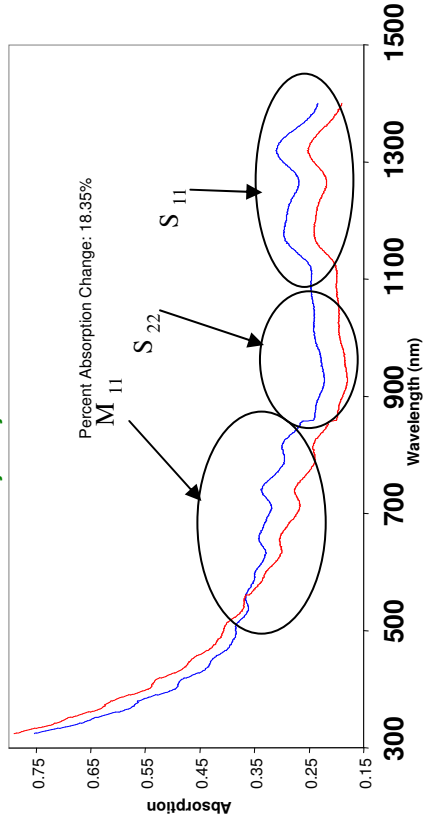
Nanotube characterization standards

Future Work



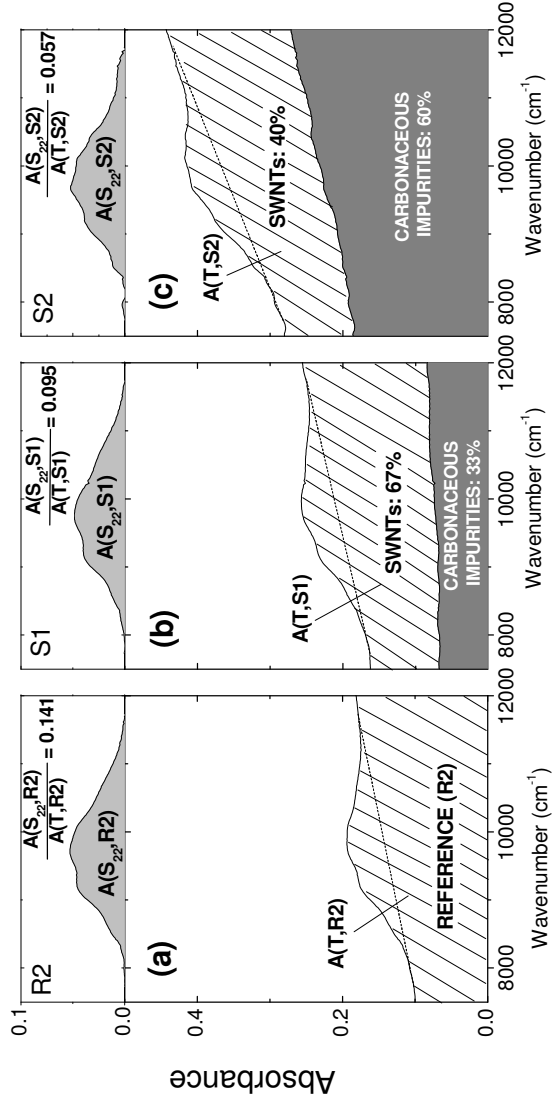
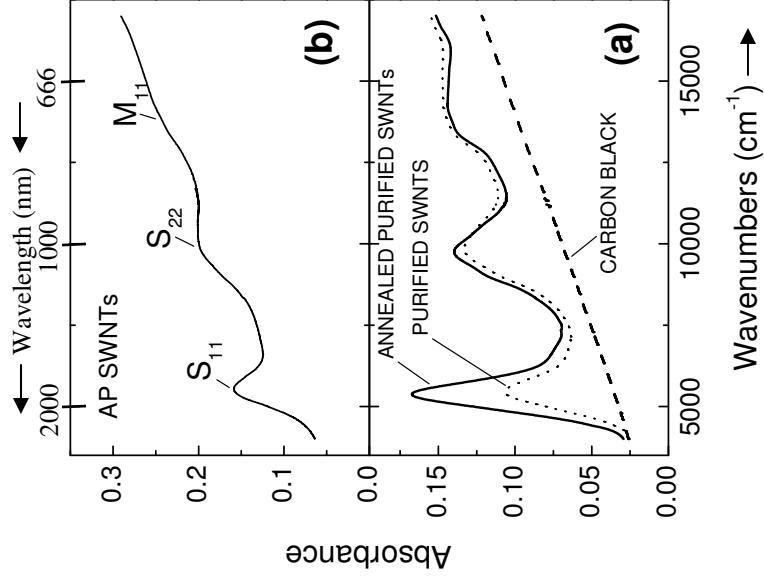
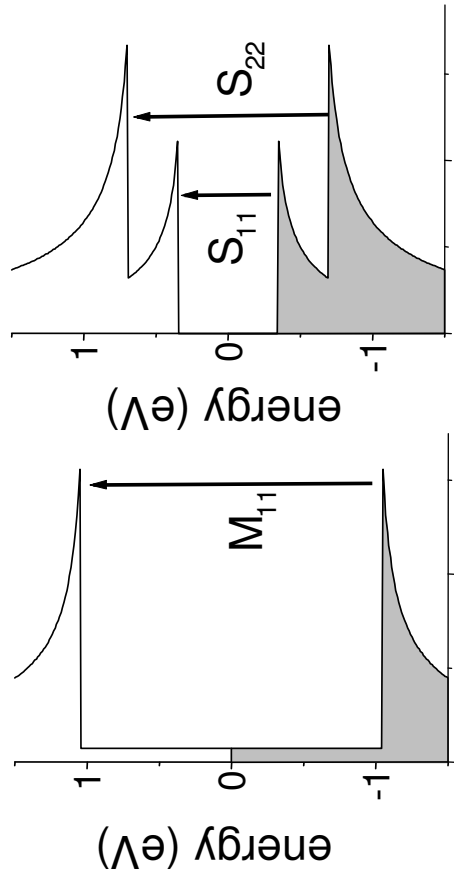
Non-nanotube Carbon by NIR Absorption

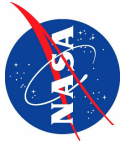
HiPco Variability Study - Back End Material



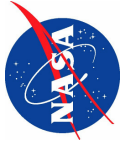
metallic

semiconducting





How do We Perform Characterization?



Macroscopic

- Thermal Gravimetric Analysis (TGA)
- UV-Visible-Near Infrared (UV-Vis-NIR) Absorption
- **NIR Fluorescence**
- Inductively Coupled Plasma (ICP)
- **Optical Microscopy**
- Dynamic Light Scattering (DLS)
- X-ray Diffraction (XRD), SAXS, SANS
- Resistivity
- Surface Area(BET)
- Tensile Strength
- Thermal Conductivity

Microscopic

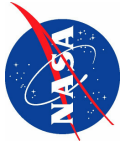
- Scanning Electron Microscopy (SEM)
- Energy Dispersive X-ray Analysis (EDX)
- Raman Spectroscopy
- X-ray Photoelectron Spectroscopy (XPS)

Nanosopic

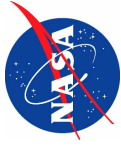
- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscopy (STM)

Purity and Dispersion





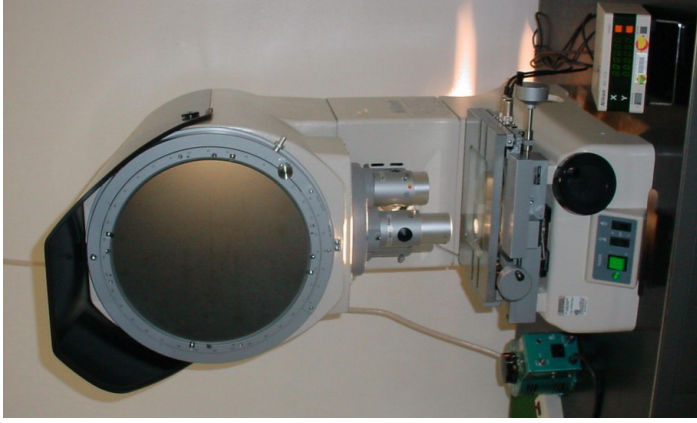
Macrodispersion and Nanodispersion



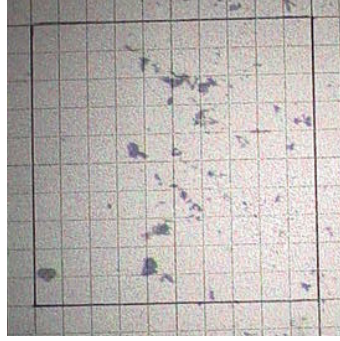
Optical Dispersion Analysis Protocol

Guidelines for a quantitative reproducible protocol:

- Follow guidelines for UV-Vis protocol and establish dispersion grade (A, B, or C).
- Once dispersion grade has been assigned, sonicate sample (0.1 mg/ mL) for 1 h.
- After 1 h of sonication, allow sample to rest at room temperature for 1 h.
- Stir sample thoroughly and remove an aliquot (17uL)
- *A volume of 17 uL was found to be ideal for full coverage by a slide cover. This volume minimized the formation of vacuoles without excess spillage outside 22mm x 22mm area.*
- Use the Optical Comparator at 100x magnification equipped with a grid to count the particle distributions within an area.
- Count an area that represents the highest concentration of particles in the sample
- Use the ODA Protocol Table to determine the dispersion grade.

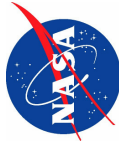


Nikon V12A Comparator



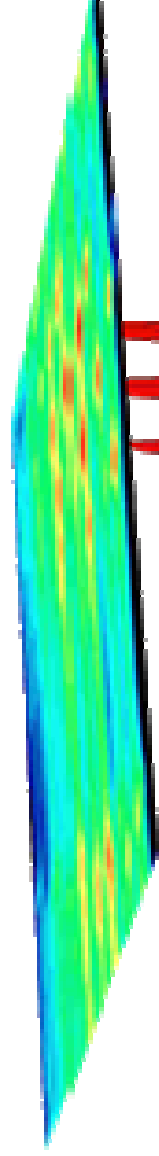
0.02"

100X



NIR Fluorescence for Nanodispersion

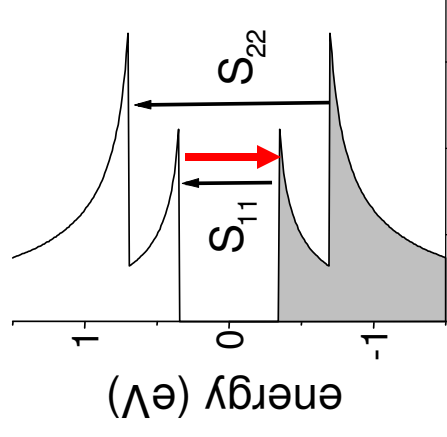
Chirality Determination



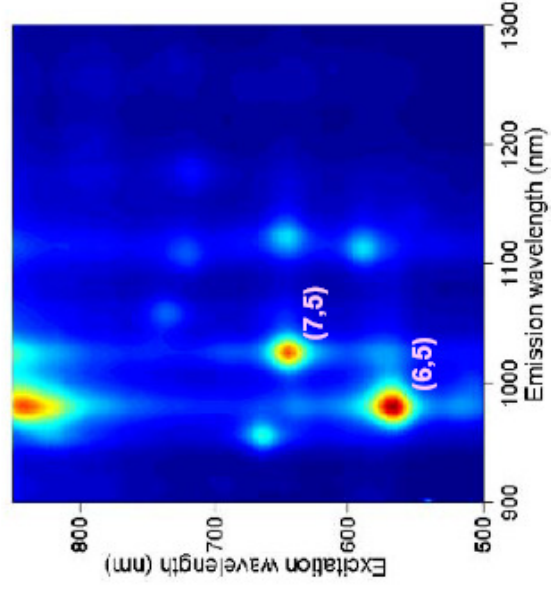
HiPco

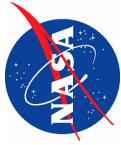
DOS

semiconducting



Alcohol CVD





Possible Additions to JSC Protocol

NIR Absorption for Purity Assessment

ODA, and NIR Fluorescence for Dispersion

AFM for Lengths and Diameters

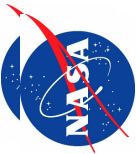
E-Beam Diffraction, STM for Chirality

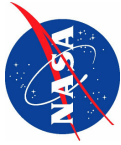
Electrical Conductivity

Thermal Conductivity

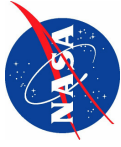
Mechanical Strength Measurements

TGA-IR/MS for Functional Group Assessment





SWCNT Measurement Challenges



Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion

Study of fine variations in harvested material

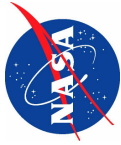
- Laser, arc and CVD production chambers

Additions to NASA-JSC protocol

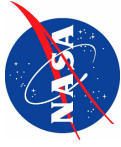
- “Non-nanotube” carbon and nanodispersion

→ **Nanotube characterization standards**

Future Work



Nanotube characterization standards



NASA-NIST Collaboration

- Purity and Dispersion Workshops 2003 and 2005**
- Practice Guides on web page**

http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide.htm

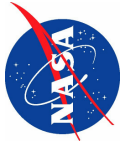
NASA-IEEE Collaboration

- Development of IEEE-P1690**

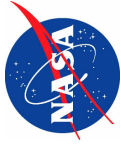
Characterization of Carbon Nanotubes Used as Additives in Bulk Materials”

NASA-ANSI-ISO Collaboration under ISO-TC229 for Nanotechnology

- Major Player in the US TAG for WG2 on Characterization**
- Responsible for characterization standards of SWCNTs**



SWCNT Measurement Challenges



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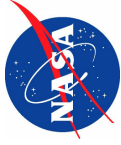
- Laser, arc and CVD production chambers

Additions to NASA-JSC protocol

- “Non-nanotube” carbon and nanodispersion

Nanotube characterization standards

→ **Future Work**

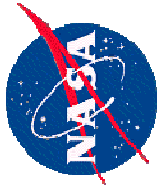


Future Work



- **Update characterization protocol for purity and dispersion of SWCNTs**
- **Identify and develop measurement standards for this characterization protocol**
 - SEM, TEM, TGA, Raman, UV-VIS-NIR**
 - Absorption, Optical Dispersion Analysis, NIR**
 - Fluorescence**

Thanks for Your Attention



Team Members



Dr. Ram Allada
Dr. Sivaram Arepalli
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Dr. Olga Gorelik
Dr. Brian Mayeaux
Dr. Pavel Nikolaev
Dr. Carl Scott
Dr. Edward Sosa
Dr. Leonard Yowell
Mr. Padraig Moloney
Mr. William Holmes
Mr. Mike Waid
Ms. Beatrice Santos



<http://mmptdpublic.jsc.nasa.gov/jscnano/>

- NASA-JSC Director's Discretionary Funds
- Jacobs Sverdrup ESC contract